Evaluation of the Emission, Transport, and Deposition of Mercury, Fine Particulate Matter, and Arsenic from Coal-Based Power Plants in the Ohio River Valley Region

Semi-Annual Technical Progress Report
for the Period October 3, 2004–April 2, 2005

to

Department of Energy
Washington, D.C.

DOE Award Number: DE-FC26-03NT41723

Award Recipient:

Ohio University
Athens, Ohio

Report Period Start Date: October 3, 2004
Report End Date: April 2, 2005

Principal Author: Kevin Crist
Ohio University

DOE Award Number: DE-FC26-03NT41723

Contractor: **Ohio University**
Institute for Sustainable Energy and the Environment
Building 21, The Ridges
Athens Ohio, 45701

Subcontractors: **CONSOL Energy**
Research & Development
400 Brownsville Road
South Park, PA 15129-9566

Advanced Technology Systems, Inc.
639 Alpha Drive—RIDC Park
Pittsburgh, PA 15238-2819

Atmospheric and Environmental Research, Inc.
131 Hartwell Avenue
Lexington, MA 02421-3126

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PROJECT ABSTRACT

Ohio University, in collaboration with CONSOL Energy, Advanced Technology Systems, Inc (ATS) and Atmospheric and Environmental Research, Inc. (AER) as subcontractors, is evaluating the impact of emissions from coal-fired power plants in the Ohio River Valley region as they relate to the transport and deposition of mercury, arsenic, and associated fine particulate matter. This evaluation will involve two interrelated areas of effort: ambient air monitoring and regional-scale modeling analysis.

The scope of work for the ambient air monitoring will include the deployment of a surface air monitoring (SAM) station in southeastern Ohio. The SAM station will contain sampling equipment to collect and measure mercury (including speciated forms of mercury and wet and dry deposited mercury), arsenic, particulate matter (PM) mass, PM composition, and gaseous criteria pollutants (CO, NOx, SO_2, O_3, etc.). Laboratory analysis of time-integrated samples will be used to obtain chemical speciation of ambient PM composition and mercury in precipitation. Near-real-time measurements will be used to measure the ambient concentrations of PM mass and all gaseous species including Hg^0 and RGM. Approximately of 18 months of field data will be collected at the SAM site to validate the proposed regional model simulations for episodic and seasonal model runs. The ambient air quality data will also provide mercury, arsenic, and fine particulate matter data that can be used by Ohio Valley industries to assess performance on multi-pollutant control systems.

The scope of work for the modeling analysis will include (1) development of updated inventories of mercury and arsenic emissions from coal plants and other important sources in the modeled domain; (2) adapting an existing 3-D atmospheric chemical transport model to incorporate recent advancements in the understanding of mercury transformations in the atmosphere; (3) analyses of the flux of Hg0, RGM, arsenic, and fine particulate matter in the different sectors of the study region to identify key transport mechanisms; (4) comparison of cross correlations between species from the model results to observations in order to evaluate characteristics of specific air masses associated with long-range transport from a specified source region; and (5) evaluation of the sensitivity of these correlations to emissions from regions along the transport path. This will be accomplished by multiple model runs with emissions simulations switched on and off from the various source regions.

To the greatest extent possible, model results will also be compared to field data collected at other air monitoring sites in the Ohio Valley region, operated independently of this project. These sites may include (1) the DOE National Energy Technologies Laboratory's monitoring site at its suburban Pittsburgh, PA facility; (2) sites in Pittsburgh (Lawrenceville) PA and Holbrook, PA operated by ATS; (3) sites in Steubenville, OH and Pittsburgh, PA operated by U.S. EPA and/or its contractors; and (4) sites operated by State or local air regulatory agencies. Field verification of model results and predictions will provide critical information for the development of cost effective air pollution control strategies by the coal-fired power plants in the Ohio River Valley region.

EXECUTIVE SUMMARY

Ohio University is performing a Cooperative Agreement with the U.S. Department of Energy's National Energy Technology Laboratory (DOE-NETL) to conduct regional-scale modeling analysis and ambient air monitoring that will provide critical information for the development of relevant and cost effective control strategies by the coal-fired power plants in the Ohio River Valley region.

The regional modeling studies will develop a comprehensive budget of arsenic, elemental mercury (Hg^0) reactive gaseous mercury (RGM), and fine particulate matter across the Ohio Valley region, including sources, sinks, atmospheric lifetimes, burdens, and advective fluxes. Updated emissions inventories for mercury and arsenic within the region will be developed to support the regional modeling studies. A comprehensive surface air monitoring (SAM) site is being developed and operated in southeastern Ohio to provide field data against which the model results can be compared. The SAM has the capability to monitor mercury speciation in ambient air and in precipitation, and it contains a full range of instrumentation for measuring the composition of fine particulate matter and co-pollutant gases. Short-term and seasonal simulations with the refined model will be compared to field measurements from the monitoring site, and the results will be used to develop a decision-support tool. A supplemental objective of the analysis is to evaluate the impacts of long-range transport from regions outside the Ohio Valley as well as biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury concentration levels in the Ohio Valley region.

The Cooperative Agreement began in April of 2003. A six month no cost extension to the original 27 month performance period has been approved. This extends the project through December of 2005. The effort has been broken down into seven separate tasks as follows:

Task 1 consists of establishing and operating the SAM site in southeastern Ohio. The SAM site has been set up and routine sampling was initiated on March 1, 2004; data collection will occur over the following 18 months.

Task 2 consists of the selection and evaluation of a 3-D regional-scale chemical transport model (CTM) for an application focused on the Ohio River Valley region. The Chemical Transport Model CMAQ (Community Multiscale Air Quality) model has been set up and is operational. A one-year base-case simulation has been completed for North America for the year 1996. An overview of the analysis of the base case simulation is presented in Section II (Experimental Design).

Task 3 involves the refinement and update of emission inventories (EIs) for sources of mercury and arsenic within and upwind of the modeled domain. The Institute for Sustainable Energy and the Environment (ISEE) plans to collect and process that emissions information into the model structure throughout the modeling effort.

Task 4 consists of short-period model runs to be made for comparison with field data. The summer of 2001 has been used for initial comparisons because of the extensive field data on particulate matter, and co pollutants available from the DOE sponsored Pittsburgh Air Quality Study. The ambient monitoring fine particulate data (PM sulfate and PM nitrate) from the Pittsburgh site and other EPA-sponsored air quality sites have been used to calibrate the short-term atmospheric chemistry model (refer to Semi-Annual Technical Report # 3). Short-term model runs for comparison with the speciated mercury and arsenic data collected at the SAM for the 2004 sampling periods will follow these initial comparisons.

Task 5 involves seasonal-scale simulations focusing on the identification of significant sources and source regions contributing to the deposition of mercury and ambient concentrations of arsenic and fine particulate matter over periods of several months or more. The modeling will also examine the efficacy of emission reduction strategies specifically for coal-fired power plants. In addition, researchers will conduct an analysis of long-range transport from regions outside the Ohio Valley and biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury in the Ohio Valley region.

Task 6 consists of the development of Web-based model interface technologies to provide industry and government agencies with a user-friendly decision-support tool to facilitate the evaluation of source-receptor relationships and the efficacy of emission reduction strategies. The framework for the Web-based GIS interface has been developed. Work on this task will continue throughout the remainder of this project.

Task 7 consists of project management, data analysis, and reporting functions.

Accomplishments and tasks completed during this reporting period include: (1) completed the analysis on base case simulation for the year 1996 with the 3-D chemical transport model (2) continued to refining and updating mercury and arsenic emission inventories for 2004; (3) operating a surface air monitoring station (SAM) at Athens, Ohio which includes sampling equipment for collecting and measuring mercury, arsenic, $PM_{2.5}$, pollutant gases, and weather data over the project period; (4) developed a GIS Web-base interface for the decision support tool.

I. INTRODUCTION

Ohio University is performing a Cooperative Agreement with the U.S. Department of Energy's National Energy Technology Laboratory (DOE-NETL) to conduct regional-scale modeling analysis and ambient air monitoring that will provide critical information for the development of relevant and cost effective control strategies by the coal-fired power plants in the Ohio River Valley Region.

Coal flue gas contains a variety of hazardous air pollutants (HAPs), including organic and inorganic chemical compounds. Among the latter, the metals mercury and arsenic are of particular concern because of their toxicity to humans and animals. An understanding of the chemistry of these elements should be the basis of proposed legislation to regulate mercury and arsenic emissions since specific chemical species will account for differences in human toxicity, rate of transport through the ecosystem, and the design variations in possible emission control schemes. An additional layer of complexity results from the fact that these elements may or may not be associated with fine particulate matter ($PM_{2.5}$ and PM_{10}) during or after emission from a stack. In general, the less volatile species such as arsenic and oxidized mercury are likely to be associated with fine particulate matter while the more volatile moieties such as elemental or reduced mercury tend to be emitted as non-associated gases. Thus, it will be necessary to determine the chemical forms of mercury and arsenic present at the stack and at designated receptor sites, and to determine the fractions of these species bound to fine particulate matter.

Mercury, fine particulate matter, and arsenic can be transported over large distances due to their minimal rate of sedimentation. In particular, mercury transport must be considered a global problem. Elemental mercury is believed to have a half-life of approximately one year in the atmosphere, and little is known about its cyclic transport between land, water, and air. Biogenic transport and biogenic sources are even less well understood. Therefore, the ISEE will adopt a regional scale approach for adequate evaluation of source-receptor relationships for mercury, fine particulate matter, and arsenic. Our approach in evaluating the impact of arsenic and mercury emissions from coal-fired power plants and other sources is to examine the source-receptor relationship through ambient monitoring and regional scale modeling.

A. Project Goal and Objectives

The overall objective of the project is to quantitatively evaluate the emission, transport, and deposition of mercury, fine particulate matter (PM), and air toxics (arsenic) in the Ohio River Valley region. This evaluation involves two interrelated areas of effort: regional-scale modeling analysis and ambient air monitoring.

The objective of the regional modeling studies is to develop a comprehensive budget of arsenic, elemental mercury (Hg^0) and reactive gaseous mercury (RGM), and fine particulate matter including sources, sinks, atmospheric lifetimes, burdens, and advective fluxes across the Ohio Valley region. To support this objective, project researchers will develop updated emissions inventories for mercury and arsenic within the region. The second objective is to develop an air-monitoring site in Athens, Ohio to provide the capability to monitor mercury in ambient air and in precipitation. Researchers will compare the refined model's short-term and seasonal simulations to field measurements from the monitoring site and use the results to develop a decision-support tool. A supplemental objective of the analysis is to evaluate the impacts of long-range transport from regions outside the Ohio Valley as well as biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury concentration levels in the Ohio Valley region.

B. Project Development (Tasks)

Seven separate tasks will be completed over a 33-month performance period. A six month no cost extension to the original 27 month performance period has been requested. The following project schedule is based on a project start date of April 3, 2003. Table 1 on page 3 presents a progress summary for each task. Section II Experimental Design is a detailed description of each task and the progress achieved toward its completion as of April 2, 2005.

Project Schedule

- Task 1 consists of establishing and operating a Stationary Ambient Monitoring (SAM) site in Athens, Ohio. Routine sampling was initiated on March 1, 2004. Data collection will occur over the following 18 months.

Tasks 2–6 comprise the modeling process, which will continue throughout the first 30 months of the project. Throughout Tasks 2–6, the project team will keep abreast of ongoing research and newly published literature pertaining to the atmospheric behavior of mercury. Whenever possible, new findings concerning mercury speciation and transport will be incorporated into the model algorithms.

- Task 2 consists of the selection and evaluation of a 3-D regional-scale chemical transport model (CTM) for an application focused on the Ohio River Valley region. The project team has completed the setup and development of the CTM grid system and a one-year base-case simulation for the year 1996 has been conducted for North America. Analysis of the 1996 simulation in presented in Section II (Experimental Design).

- Task 3 involves the refinement and update of emission inventories (EIs) for sources of mercury and arsenic within and upwind of the modeled domain. It is anticipated that information on emissions will continue to be collected and processed into the model structure throughout the modeling effort.

- Task 4 consists of conducting short-period model runs for comparison with field data. A short-term modeling run has been completed for July 2001 for the eastern United States. The model run was conducted with the photochemical model CMAQ. The project team used particulate sulfate and nitrate data collected during the summer of 2001 from the DOE funded Pittsburgh Air Quality Study for initial comparisons. In addition short-term model runs for comparison with the speciated mercury and arsenic data collected at the Athens SAM for the 2004 sampling periods will be conducted.

- Task 5 involves seasonal-scale simulations that focus on the identification of significant sources and source regions contributing to the deposition of mercury and ambient concentrations of arsenic and fine particulate matter over periods of several months or more. The modeling will also examine the efficacy of emission reduction strategies specific to coal-fired power plants. In addition, researchers will analyze the long-range transport from regions outside the Ohio Valley and the biospheric recycling of elemental Hg on the measured and modeled reactive and total mercury in the Ohio Valley Region.

- Task 6 consists of the development of Web-based model interface technologies to provide industry and government agencies with a user-friendly decision-support tool to facilitate the evaluation of source-receptor relationships and the efficacy of emission reduction strategies. The frame work for the GIS Web interface has been completed. The development of the Web-based system will continue through the remainder of this project.

- Task 7 consists of project management, data analysis, and reporting functions.

Table 1 below is a progress summary for each task.

Table 1. Progress summary

Task #	Description	Planned % Completed	Actual % Completed
1	SAM	100	75
2	Base Case Simulation	100	100
3	Emission Inventories	100	70
4	Model Comparison	100	50
5	Seasonal Scale Simulations	100	20
6	Development of Support Tool	100	10
7	Project Management	100	50

II. EXPERIMENTAL DESIGN

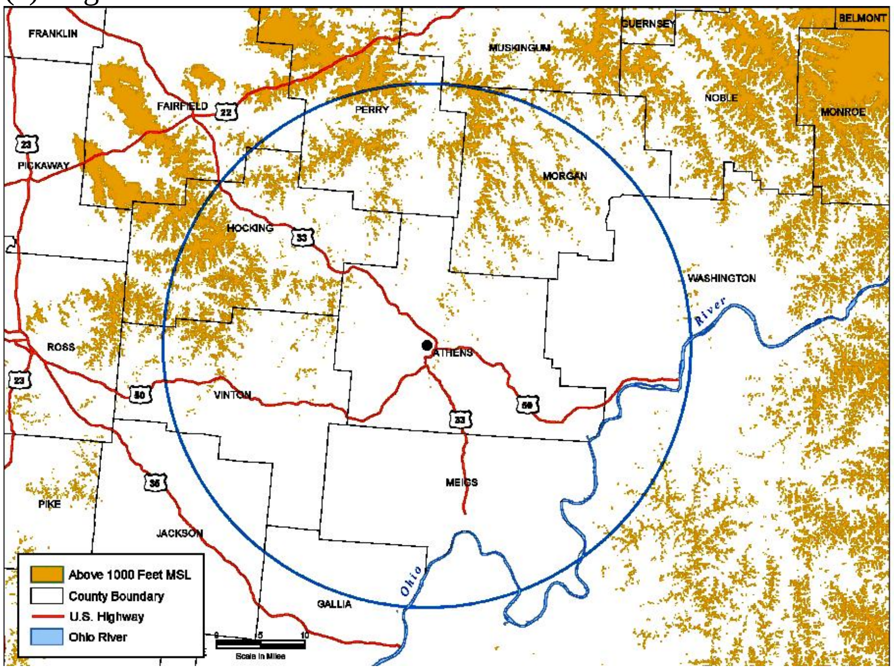
In this section, the description of each task is presented as it was proposed in the funding application. Following the description is a discussion of the progress made toward completing the task.

Task 1 - Establish and operate a (SAM) station in Athens, Ohio

The proposal for this project designated that the ISEE would establish a SAM station in Steubenville, Ohio. However, prior to April 3, 2003 the Environmental Protection Agency set up a SAM station in Steubenville that has the capacity to monitor for mercury. Consequently, the ISEE was able to select another site for the SAM station proposed for this project. The project staff located an optimal site south of Athens, Ohio in the heart of the Ohio River Valley. At an elevation of 950 feet, the site is the highest point within a 100-mile radius to the east, south, and west (Figure 1, page 4). It is an excellent site from which to capture the transport of pollutants into and out of the valley. In addition, a 350-foot communication tower is adjacent to the site. ISEE has installed a wind-speed and wind-direction sensor atop the tower that will provide critical information for evaluating transport events.

NOTE: Consol Energy R&D is involved with Task 1 under subcontract to Ohio University. The subcontract was not executed until August 5, 2003, which delayed Task 1 by several months.

(a) Regional



(b) Local

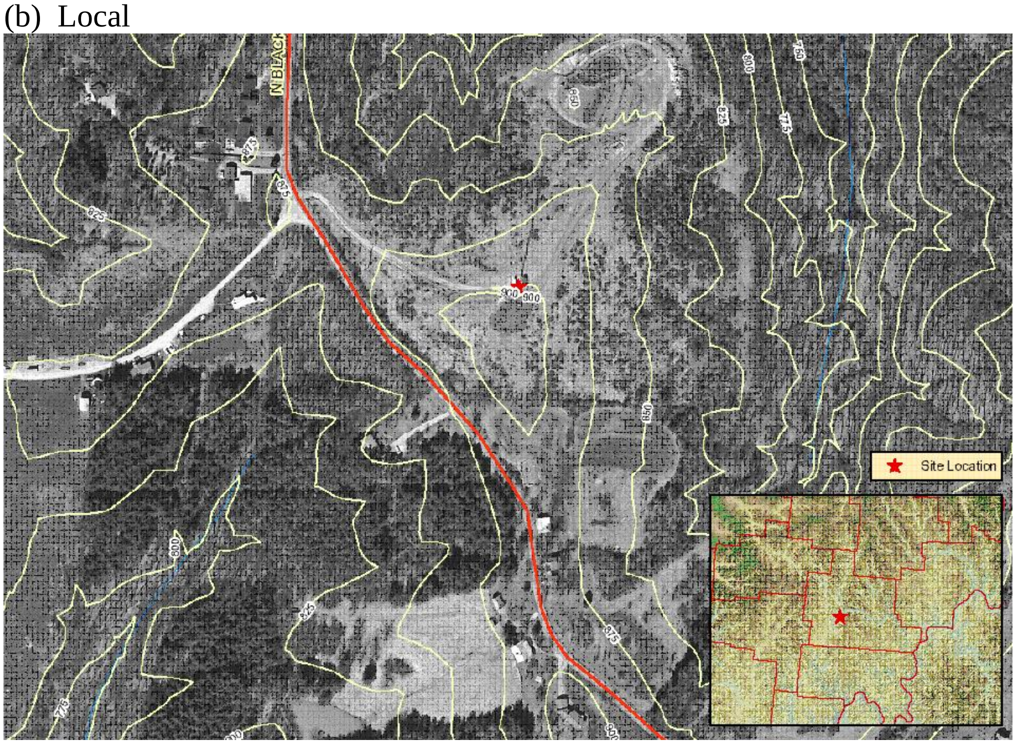


Figure 1. Topographical map of the Athens site: (a) regional and (b) local

The Athens site utilizes air-monitoring equipment from the Steubenville Comprehensive Air Monitoring Project (SCAMP), sponsored by DOE-NETL under Cooperative Agreement DE-FC26-00NT40771. In addition, the site includes sampling equipment to collect and measure mercury, including total, elemental, reactive, particulate, and wet/dry deposition.

Task 1 accomplishments from October 3, 2004 to April 2, 2005:

There were two primary objectives during this period:

- Maintain instrument operation
- Enhance data QA/QC recovery

Accomplishments: By month:

October and November

- In the last week of November the Tekran started giving high zeros and bad data. The cooling fan on the 1130 module was running continuously which reduced the temperature during desorb cycle from 500^{o} C to 330^{o} C.

December

- Presented preliminary data/analysis at the Ohio Air Quality and Coal Research Symposium
- The Speciation and the FRM samplers, as well as the ammonia denuder sampler were operating properly. The FRM was beginning to experience automation controller slippage, the unit was given manual assistance during carousel oscillations. The FRM was calibrated on December 16.
- The gas analyzers operated properly on 28 of 31 days in December. Maintenance included the replacement of the savillex filters on two occasions and manual adjustments immediately when necessary. The performance of the analyzers was checked every two days by comparing the calibration drift to the acceptable limits. Manual calibrations were performed once for NO_x and once for O_3 analyzer.
- Several power failures occurred around the Christmas holiday, however no major problems resulted from the power failures.
- The Tekran experienced operational problems throughout December. The amplifier controlling the denuder cooling fan malfunctioned in the 1130 unit, causing the fan to run continuously. Personnel from Computer Network Services at Ohio University were consulted for soldering and micro electronic repair. The 1130 was repaired on December 22. Electrical problems on the 2537A analyzer were also experienced. The 2537A was sent to Tekran on December 7 and was returned to operation on December 28.

January

- Speciation, FRM, as well as the ammonia denuder sampler operated properly. For two days the zero air generator in the trailer malfunctioned due to a faulty relay.
- During the week of 11th, the wet deposition sampler was blown over during a storm. The meter box was replaced with a new one and the sample collection glass ware was re-installed according to the schedule.
- The Tekran did well during the month. Regular maintenance and calibrations were performed according to the weekly and monthly schedules.

February, March

- The FRM and speciation monitor both experienced operational problems during February and March. The FRM's automation control is not working which prevents loading of the filter. The speciation monitor's display is exhibiting illogical flows. Significant time was invested to try to identify and solve the problems. However, Thermo Analytic has been extremely unresponsive and difficult to get resolution on these issues. Efforts will continue to resolve these problems.

Additional Items:

- Focused efforts by Ohio University and CONSOL Energy R&D reduced almost all of the sampling data (Tekran, TEOM, gases, meteorological, mercury deposition, FRM, and Speciation through the end of February 2005. This brings the majority of the data validation and data reduction phases current. While completing these tasks some key measurement issues were addressed (e.g. inclusion of negative TEOM data as per R&P's advice and comparison of PM2.5 concentrations collected on the TEOM vs. the FRM and Speciation samplers).
- A site audit was scheduled with the National Ambient Mercury Deposition Network for April 2005. ATS, the network's site auditor, will perform the audit.
- As of the end of March 2005, analytical activities included.
  - 42 denuders have been coated for mercury sampling.
  - Approximately 1100 filters have been pre and post weighed from PM sampling.
  - Approximately 240 quartz filters were analyzed for carbon species
  - Approximately 130 Teflon filters were extracted and analyzed for ions
  - Trace elements analysis has not started. Trace element analysis is planned for June 2005 once a few method issues are resolved.

Task 2 - Evaluate and Select a 3-D Regional-Scale Atmospheric Chemical Transport Model (CTM) and Conduct a Base-Case Simulation

Several 3-D regional-scale CTMs with the ability to simulate tropospheric ozone, visibility, and fine particulate matter are appropriate for application to the Ohio River Valley region to evaluate total fine particulate matter mass and the arsenic component of fine particulate matter. The ISEE and Atmospheric and Environmental Research (AER) have established the 3-D modeling framework. AER completed a base-case model simulation for the year 1996.

The project team chose the Community Multi-Scale Air Quality (CMAQ) model for air-pollution studies on a regional scale for this study. The EPA and its collaborators (Byun & Ching, 1999) developed the CMAQ, which uses non-hydrostatic Penn State/NCAR mesoscale model (MM5) V3-derived dynamics for transport.

Task 2 accomplishments from October 3, 2004 to April 2, 2005 :

- Conducted an annual simulation for 1996 using the modified CMAQ-Hg code with the MEBI chemistry solver. The modeling year was divided into four 3-month periods (Jan-Mar, Apr-Jun, Jul-Sep, Oct-Dec) and 3-month simulations were conducted on different processors to speed up the overall completion of the annual simulation. A 10-day spin-up cycle was used for each 3-month simulation period. Each simulation day requires about 3 hours of CPU time.
- The seasonal boundary conditions from the global mercury chemistry transport model were applied as follows for the 3-month simulation periods:
  - Winter boundary conditions: January, February, and December
  - Spring boundary conditions: March, April, and May
  - Summer boundary conditions: June, July, and August
  - Fall boundary conditions: September, October, and November
- The version of the CMAQ-Hg code used in these simulations also included modifications to calculate and save the daily cumulative dry and wet deposition amounts and daily average concentrations of Hg (the default model only saves the hourly values).

Over view of the modeling results

Figure 2 illustrates the modeled dry, wet, and total (i.e., dry plus wet) mercury deposition fluxes in the 1996 base case simulation. The mercury dry deposition fluxes shown exclude Hg(0) which is not modeled in CMAQ-Hg. Simulated annual dry deposition ranges typically between 5 and 25 $\mu g/m^2$ east of the Mississippi river. Dry deposition fluxes are highest in the northeastern United States resulting from the impacts of local/regional emission sources. The highest simulated dry deposition is 174 $\mu g/m^2$ near Baltimore, MD resulting from a combination of high local emissions (e.g., municipal waste incinerator), regional contributions, and global background. Isolated areas in the upper Midwest and in New Jersey, Maryland, Pennsylvania, and New England experience mercury annual dry deposition exceeding 50 $\mu g/m^2$. The Geyser area north of the San Francisco Bay in California also shows high dry deposition (values exceeding 75 $\mu g/m^2$) because of Hg emissions associated with hydrothermal activity.

Simulated annual wet deposition is between 10 and 20 $\mu g/m^2$ in most of the eastern United States. Wet deposition fluxes are higher in parts of Florida, and in urban areas such as Detroit, along the Ohio River valley, and in the northeastern United States. The high fluxes result from the influence of local/regional sources (e.g., in the Northeast) or high precipitation (e.g., in Florida).

The total deposition fluxes reflect the characteristics mentioned above for the dry and wet deposition fluxes. They are mostly in the range of 20 to 50 $\mu g/m^2$ with some areas exceeding 50 $\mu g/m^2$.

Performance Evaluation of the Base Case Simulation

The annual Hg wet deposition fluxes simulated with CMAQ-Hg for 1996 were compared with measurements at the Mercury Deposition Network (NADP/MDN, 2004) stations for which data were available for 1996. Figure 3 shows the locations of the MDN mercury wet deposition measurement stations. There were eleven stations (marked in red) that were operational for all of 1996. Figure 4 presents a comparison of measured and simulated annual Hg wet deposition fluxes ($\mu g/m^2$-yr) at these eleven sites. The model overestimates wet deposition at nine sites and underestimates at only two locations (one station each in Florida and Wisconsin). The largest over predictions occur in North Carolina, South Carolina and Texas. Figure 5 shows a scatter diagram of simulated and measured wet deposition fluxes with a coefficient of determination (r^2) of 0.23, a normalized absolute error of 56%, and a normalized bias of 43% (normalized error = $\frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_i - O_i}{O_i}\right|$; normalized bias = $\frac{1}{N}\sum_{i=1}^{N}\left(\frac{P_i - O_i}{O_i}\right)$ where P_i = prediction, O_i = observation; N: number of samples).

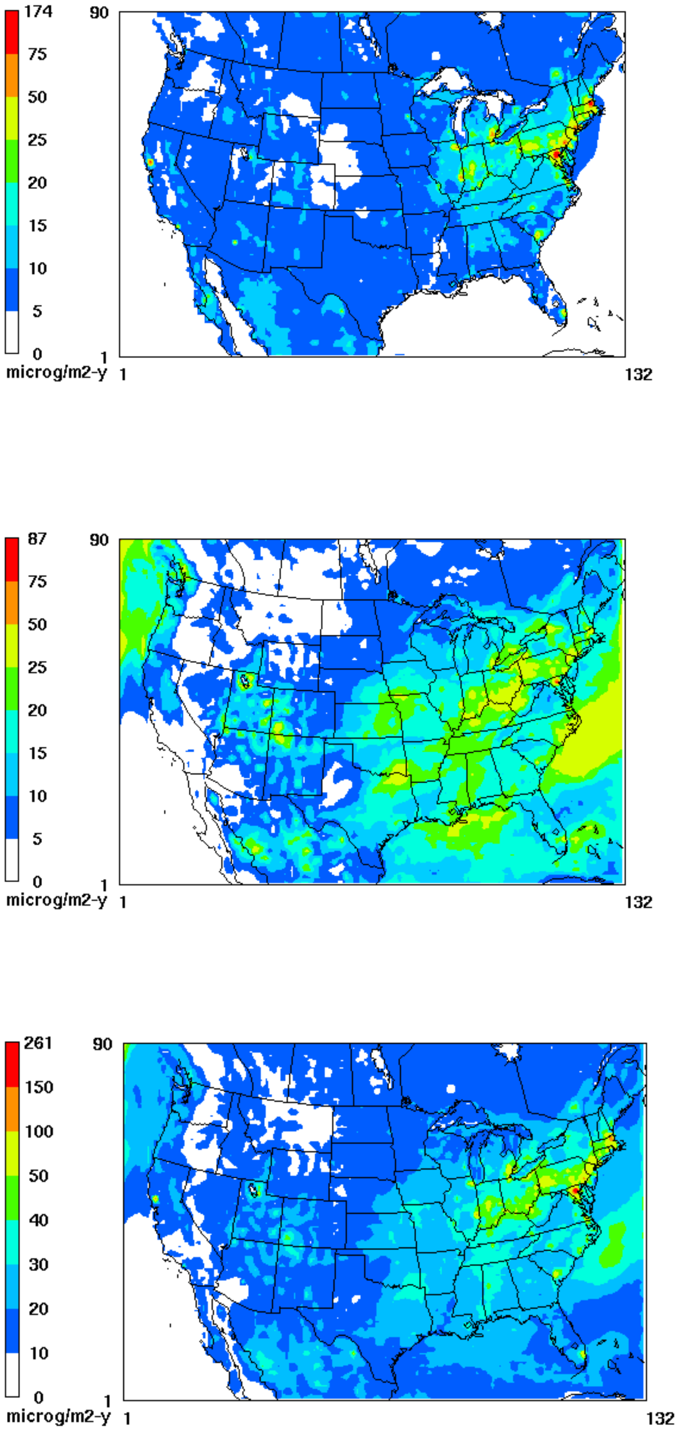


Figure 2 Simulated annual mercury deposition fluxes in 1996 ($\mu g/m^2$-yr): dry deposition (top), wet deposition (middle), and total deposition (bottom).

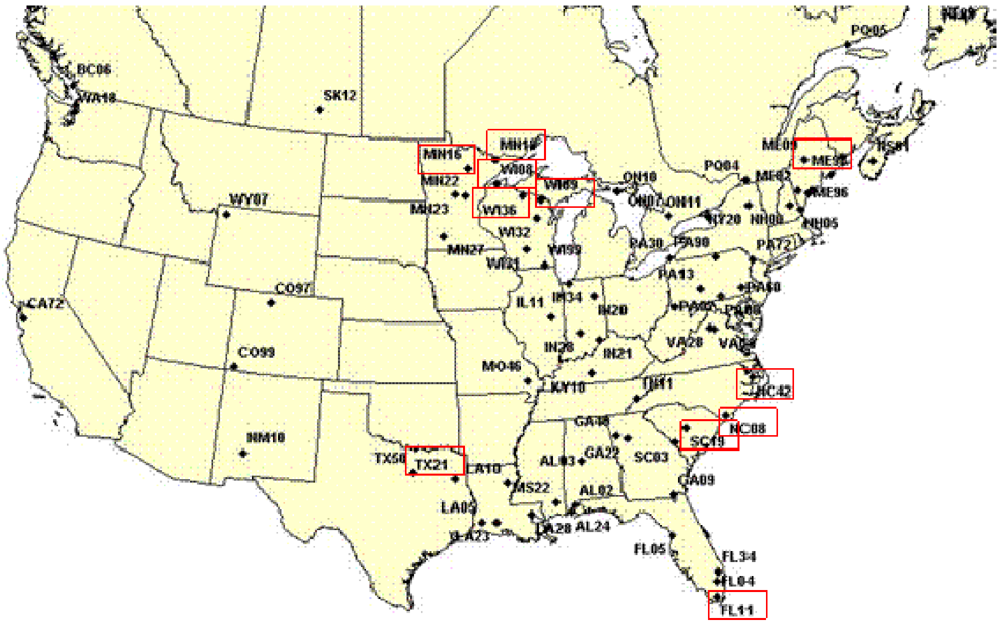


Figure 3 Wet deposition measurement sites in the Mercury Deposition Network (NADP/MDN, 2004). Sites operational for all of 1996 are marked in red.

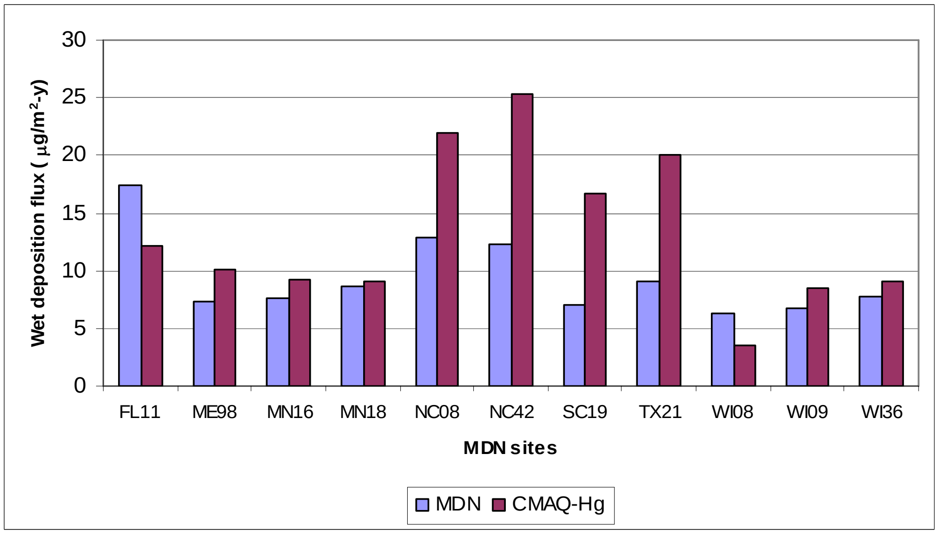


Figure 4 Comparison of measured and simulated annual Hg wet deposition fluxes (μg/m^2-yr) at the eleven MDN stations for 1996.

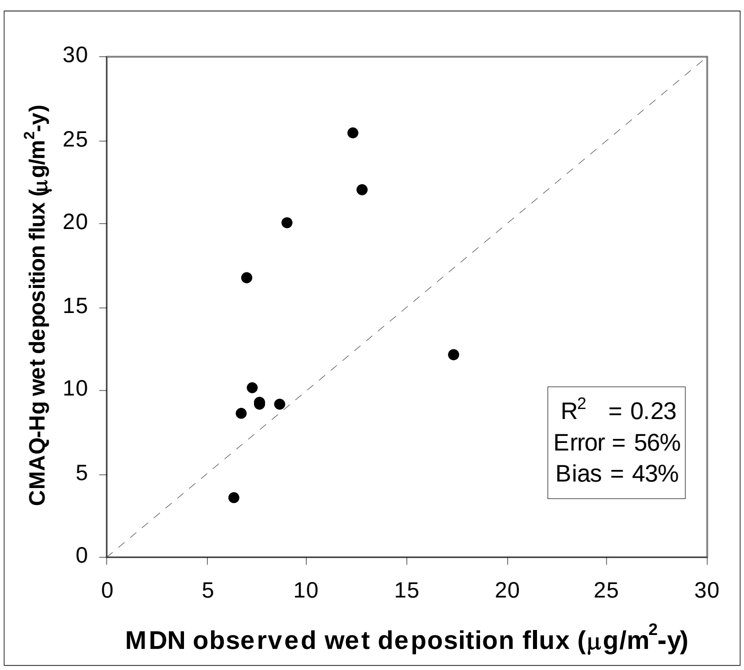


Figure 5 Scatter plot of measured and simulated annual Hg wet deposition fluxes (μg/m^2-yr).

Impact of Precipitation Fields on Model Performance

The model overestimates mercury wet deposition at most MDN stations. Since wet deposition is influenced significantly by precipitation, we examined the impact of precipitation fields on model performance. Table 2 presents a comparison of CMAQ and measured annual precipitation at the eleven MDN sites in 1996. The MM5-derived precipitation input to CMAQ-Hg is higher than the measured precipitation at all eleven NADP/MDN stations. Thus, the overestimation in wet deposition is due, in part, to differences between measured precipitation in the NADP network and modeled MM5-CMAQ precipitation, particularly in the Carolinas and Texas.

Figure 6 presents a comparison of measured and simulated annual Hg wet deposition fluxes ($\mu g/m^2$-yr) at the MDN sites after scaling by the observed/simulated precipitation ratio. Figure 7 shows a scatter diagram of simulated and measured wet deposition fluxes after performing the same scaling. Comparisons of Figures 4 and 6 and of Figures 5 and 7 show that scaling of the simulated wet deposition to account for these differences resulted in considerable improvement in model performance; the normalized absolute error was halved from 56% to 28%, the normalized bias decreased from 43% to 7% and the coefficient of determination improved from 0.23 to 0.31.

Table 2 Comparison of modeled and measured annual precipitation at the eleven MDN sites in 1996

MDN site	CMAQ precipitation (cm/yr) (from MM5)	Observed precipitation (cm/yr) (from MDN)
FL11	132	123
ME98	122	120
MN16	92	75
MN18	93	65
NC08	202	111
NC42	220	134
SC19	115	82
TX21	165	97
WI08	66	63
WI09	80	71
WI36	89	88

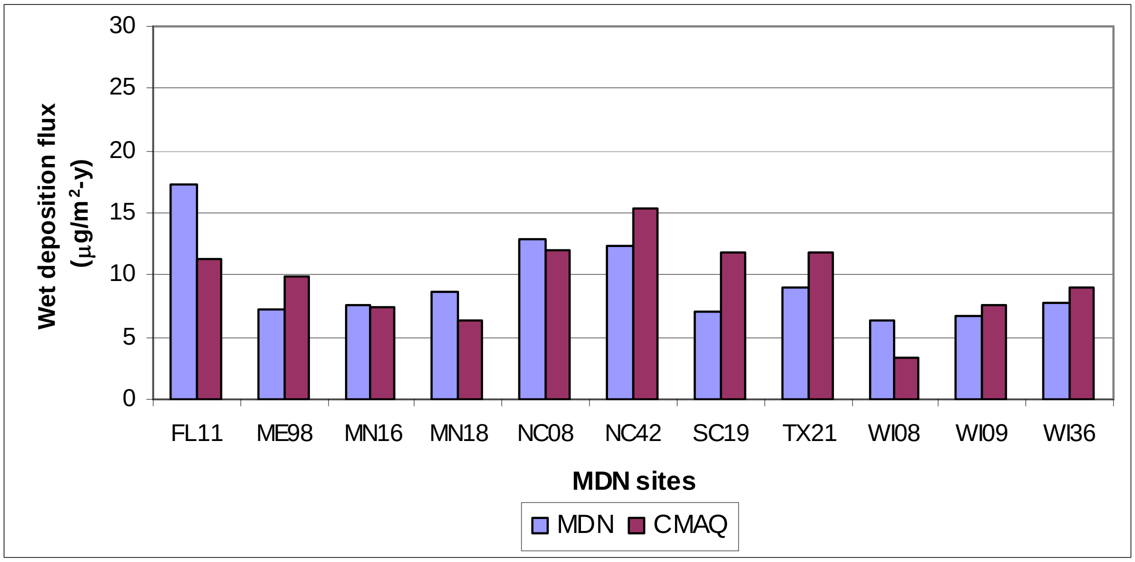


Figure 6 Comparison of measured and simulated annual Hg wet deposition fluxes (μg/m^2-yr) after scaling by observed/simulated precipitation.

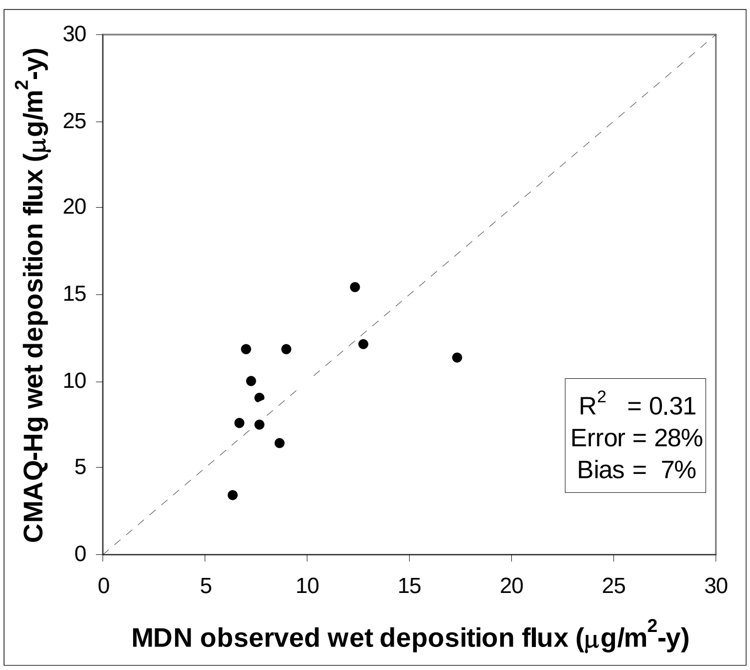


Figure 7 Scatter plot of measured and simulated annual Hg wet deposition fluxes (μg/m^2-yr) after scaling by observed/simulated precipitation.

Task 3 - Refine and Update Emission Inventories (EIs)

Advanced Technology Systems, Inc. (ATS) is enhancing the mercury and arsenic emission inventories.

Task 3 accomplishments from October 3, 2004 to April 2, 2005:

- Continued the refinement of the mercury emissions. ATS is currently working with Ohio University to integrate the updated mercury emissions into the emission inventories for CMAQ simulations.

Task 4 - Perform Short-Period Model Runs for Comparison with Field Data

ISEE will conduct a series of model runs to evaluate the system against field observations. The model run will correspond to the NETL-sponsored intensive sampling campaigns centered in Pittsburgh, Pennsylvania. Researchers will combine the extensive datasets collected during this campaign with other relevant datasets in this region. Meteorological input data for these simulations will be derived diagnostically using MM5 V3. The model evaluations will involve short-time-period runs for the field-intensive periods, storing hourly averaged fluxes and production-and-loss rates for ozone, hydrocarbons, arsenic, Hg^0, and RGM for direct comparison with field data. In addition, long-range transport events will be identified from the short-term CTM runs and evaluated with the observational data set.

In addition to the model evaluations conducted from field observations obtained from the 2001 NETL-sponsored sampling campaigns, the model will be set up and evaluated against the observational data sets, including the speciated mercury and arsenic data collected at the Athens SAM for the 2004 sampling period. These simulations will be vital for model verification because the Athens SAM will be one of the few sites providing measurements on individual mercury species and arsenic. The model evaluations will involve short-time-period runs for the field-intensive periods, storing hourly averaged fluxes and production-and-loss rates for ozone, hydrocarbons, arsenic, Hg^0, and RGM for direct comparison with field data. In addition, long-range transport events will be identified from the short-term CTM runs and evaluated with the observational data set.

Task 4 accomplishments from October 3, 2004 to April 2, 2005:

- Work is underway to perform regional and urban modeling simulations for 36-, 12-, and 4-km-grid resolutions for the year 2004. The 36-km grid will cover most of Eastern United States, whereas the 4-km domain will cover all the power plants in the Ohio River Valley region.
- The chemical transport model CMAQ has been evaluated using hourly and mean particulate sulfate and nitrate observations for the time period of July 2001. The hourly sulfate and nitrate observational data were obtained from the DOE-sponsored super site at

Pittsburgh and the mean sulfate and nitrate data were obtained from EPA sponsored air quality sites in and around the Pittsburgh region.

- The meteorological inputs were obtained from EPA's 2001 MM5 simulations and the processed emission inputs were based on EPA's 2001 National Emissions Inventory. The spatially and temporally varying lateral boundary conditions for each day of the modeling simulation were obtained from EPA. These boundary conditions were generated by EPA using a global atmospheric model.

Task 5 accomplishments from October 3, 2003 to April 2, 2005:

- The project staff has completed a one-year base case simulation for 1996. The research team is currently preparing for the 2004 sensitivity evaluations. Further work on this task is slated for a later phase of the project.

Task 6 - Development of a Decision-Support Tool

ISEE will conduct a series of model runs to perform a matrix analysis of the sensitivity of point sources to deposition patterns in the region. The analysis will also include selective emission reduction scenarios for these point sources. The team will couple this matrix with a GIS and the emission pre-processor to provide a detailed spatial analysis of the source–receptor relationships. In addition, this entire system will be supported by Web-based technologies to provide industry and government agencies with a user-friendly decision-support tool that will evaluate source-receptor relationships and the efficacy of emission reduction strategies.

Task 6 accomplishments from October 3, 2004 to April 2, 2005:

The frame work for the web-based support tool has been completed. An interactive web based GIS interface linking sources with a data base which will contain the results from the matrix analysis was developed. The Web-based system will provide a user-friendly interface linking specified source reductions with the associated impact on receptor sites.

Task 7 - Project Management, Data Analysis, and Reporting

This task involves all communication between the project team members, DOE-NETL, and external collaborating parties and includes all meetings, presentations, and DOE-required reports pertaining to the project. To facilitate data analysis, the data from the SAM and the results of the model runs will be archived into a user-friendly database that will provide functionality to help calculate final mercury, arsenic, and fine particulate matter mass and composition concentrations. It will also allow the delineation of basic trends and the evaluation of variables. To the greatest extent possible, the data from the SAM site will be incorporated into the ambient air quality database being compiled for DOE-NETL by ATS and Ohio University under project DE-FC26-02NT41476. However, the primary function of the database will be to reduce data efficiently for evaluation of the proposed model simulations. At the conclusion of the project, Ohio University will submit the database containing the SAM information, results of model runs, and comparison statistics to DOE-NETL along with a comprehensive final report.

Task 7 accomplishments from October 3, 2004 to April 2, 2005:

- Presentation at Ohio Air Quality and Coal Research Symposium, Athens, OH, December 3, 2004.

- Presentation at Particulate Matter Supersites Program and Related Studies, AAAR International Specialty Conference, Atlanta, GA, February 11, 2005.

- Meet with David Streets and Rao Kotamarthi at Argonne National Laboratory to discuss the potential for incorporation of their mercury emission inventories for China into the model simulations for this project. Their participation would be partially supported under an Environmental Protection Agency proposal currently under review.

- An abstract for an oral presentation at the Air Quality V conference was submitted. The conference will be held in Arlington, Virginia in September 2005. A proceedings paper is required for oral presentations and the paper is due on August 1, 2005.

- An abstract for an oral presentation was accepted at the Air and Waste Management Annual Conference in June 2005. Data from the SAM will be presented.

III. SUMMARY OF RESULTS

The Cooperative Agreement began on April 3, 2004. A six month no cost extension was requested which will extend the project through December, 2005. During the fourth reporting period of this project (October 3, 2004 – April 2, 2005) Consol and ISEE continued the operation of the SAM site.

The ISEE researchers chose the CMAQ model developed for air-pollution studies on a regional scale by the EPA and its collaborators. AER has accomplished the 1-year run for the 36-km-grid domain for 1996 using CMAQ.

Model performance for the 1996 simulation was conducted by comparing predicted annual wet deposition fluxes with 1996 data from the Mercury Deposition Network. CMAQ-Hg overestimated mercury wet deposition at nine of the eleven MDN stations in 1996. This overestimation was due, in part, to differences between measured precipitation in the NADP network and modeled MM5-CMAQ precipitation, particularly in the Carolinas and Texas. Scaling of the simulated wet deposition to account for these differences resulted in considerable improvement in model performance; the normalized absolute error decreased from 56% to 28%, the normalized bias dropped from 43% to 7% and the coefficient of determination (r^2) increased from 0.23 to 0.31.

ATS is continuing to upgrading the mercury and arsenic emission inventory files. The focus of their efforts is to develop a comprehensive and accurate emission inventory utilizing current research on emissions data from coal-fired power plants. The ISEE has initiated work on the short-scale simulations for 2004 and developed a GIS interface for the decision support tool.

IV. CONCLUSIONS

The initial phase of the project was delayed by approximately three months due to contract negotiations with the subcontractors. However, the monitoring efforts and the modeling efforts have been initiated and are proceeding as expected.

REFERENCES

Byun, D. and J. Ching, 1999: Introduction to the Models-3 framework and the Community Multiscale Air Quality Model (CMAQ). In *Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System*, EPA/600/R-99/030, U.S. Environmental Protection Agency, Washington, D.C

Mebust et al. 2003: Models-3 Community Multiscale Air Quality (CMAQ) Model Aerosol Component. 2. Model Evaluation. *Journal of Geophys Res*. 108: 4-1 - 4-18.